Synthesis, Fluxional Behaviour, and Oxidative-addition Reactions of some μ-Alkylthio-diplatinum(II) Complexes

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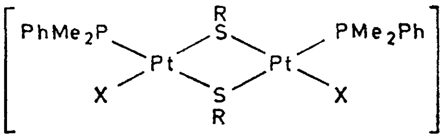
A series of complexes *cis*-$[Pt_2X_2(PMe_2Ph)_2(\mu\text{-}SMe)_2]$ (X = Cl, I, Me, or Ph) and *cis*-$[Pt_2X_2(PMe_2Ph)_2(\mu\text{-}SEt)_2]$ (X = Cl or Me) has been prepared. The complexes undergo a fluxional process thought to involve inversion at the bridging sulphur atoms, and the rate is strongly dependent on the group X. Reactions of the complexes with X = Me or Ph with methyl iodide are complicated and involve oxidative-addition–reductive-elimination sequences to give monomeric organoplatinum complexes as the final products.

OXIDATIVE-ADDITION reactions of organoplatinum(II) complexes and reductive-elimination reactions of organoplatinum(IV) complexes have been studied closely in recent years.[1-5] The great majority of this work has been concerned with mononuclear complexes. In this paper the synthesis of some dimeric thio-bridged organoplatinum(II) complexes and a study of their fluxional behaviour in solution and of their reactions with methyl halides are reported. It has previously been reported [6] that reaction of chlorine with *trans*-$[Pt_2Cl_2(\mu\text{-}Cl)_2(PPr^n{}_3)_2]$ gives the product of oxidative addition, $[Pt_2Cl_6(\mu\text{-}Cl)_2(PPr^n{}_3)_2]$.

RESULTS

Preparation of the Complexes.—Reaction of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$ [7] with methanethiol gave *cis*-$[Pt_2Cl_2(PMe_2Ph)_2(\mu\text{-}SMe)_2]$, which underwent metathesis reactions with sodium iodide, methyl-lithium, or phenylmagnesium bromide to give *cis*-$[Pt_2X_2(PMe_2Ph)_2(\mu\text{-}SMe)_2]$ when X = I, Me, or Ph respectively. Similar complexes with bridging ethylthio-groups were also prepared. The complexes with the strongly bridging alkyl thio-ligand were chosen in order to obtain stable methyl- and phenyl-platinum derivatives.[8] The complexes were all stable in air and could be stored at room temperature without decomposition.

N.m.r. Spectra of the Complexes.—The structures of the complexes *cis*-$[Pt_2X_2(PMe_2Ph)_2(\mu\text{-}SMe)_2]$, (1a)—(1e), were deduced from the ^1H n.m.r. spectra.[9] Thus two signals due to the SMe groups *cis* and *trans* to the phosphine were observed. Only the SMe protons *trans* to phosphine showed coupling to ^{31}P (giving a 1 : 2 : 1 triplet resonance), while the SMe protons *cis* to phosphine appeared as a singlet. The bridging nature of the SMe groups is confirmed by the observation of satellites due to coupling with ^{195}Pt ($I = \frac{1}{2}$, natural abundance 34%). Thus an SMe group bridging two equivalent Pt nuclei gives rise to a 1 : 8 : 18 : 8 : 1 quintet, with spacings of $\frac{1}{2}\,{}^3J(PtH)$.[9] This pattern was observed for all the complexes, although the weak outer lines which arise from the $M_I = \pm 1$ lines of the molecules with two ^{195}Pt atoms (natural abundance 11%) could not always be detected due to the limited solubility of the complexes. For a terminal SMe group the usual 1 : 4 : 1 triplet, with the outer lines due to coupling with a single ^{195}Pt nucleus, would be expected. Details of the n.m.r. spectra are given in Table 1.



(1)

X	X	R
a;	Cl	Me
b;	I	Me
c;	Me	Me
d;	Ph	Me
e;	Cl	Et
f;	Me	Et

Further structural information can be obtained from the methylphosphorus resonances. For the planar complex $[Pt_2Cl_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$ a doublet was observed for the PCH_3 protons due to coupling with ^{31}P, but in the complexes *cis*-$[Pt_2X_2(PMe_2Ph)_2(\mu\text{-}SR)_2]$, (1a), (1b), and (1e), two such doublets were observed. This is due to the absence of a plane of symmetry containing the Pt–P axis which leads to non-equivalence of the methyl groups on each phosphine.[2] On warming the solutions the two doublets coalesced to give one doublet; the coalescence temperatures were 40—45 °C for (1a), 46—48 °C for (1b), and 45—50 °C for (1e) in 1,1,2,2-tetrachloroethane solution at 60 MHz. Only one methylphosphorus doublet was observed at temperatures down to −100 °C for (1c), (1d), and (1f). The same features were observed in the ^{13}C n.m.r. spectra. Thus the ^{13}C n.m.r. spectra of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$ contained one doublet at δ 12.5 p.p.m. due to PCH_3 carbon atoms [$^1J(PC)$ 47, $^2J(PtC)$ 40 Hz]. However, the ^{13}C n.m.r. spectrum of *cis*-$[Pt_2Cl_2(PMe_2Ph)_2(\mu\text{-}SMe)_2]$ contained two resonances, due to PCH_3 carbon atoms at δ 12.1 [$^1J(PC)$ 41, $^2J(PtC)$ 29 Hz] and 12.7 p.p.m. [$^1J(PC)$ 40, $^2J(PtC)$ 34 Hz]; *cis*-$[Pt_2Me_2(PMe_2Ph)_2(\mu\text{-}SMe)_2]$ gave only one such resonance at δ 13.3 p.p.m. [^1J (PC) 39, $^2J(PtC)$ 34 Hz].

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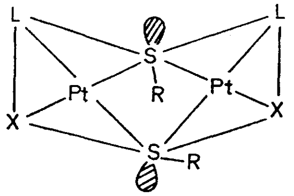
The structure of the complex $[Pt_2Cl_2(PPr_3)_2(\mu\text{-}SEt)_2]$ has been determined by *X*-ray diffraction to be (2; X = Cl, R = Et, L = $PPr^n{}_3$).[10] The angle between the co-ordination planes of the platinum atoms is 130°, while the SEt



(2)

groups adopt the *anti* configuration. In order for the two methylphosphorus doublets in (1) to coalesce in the n.m.r. spectrum it is necessary that an effective plane of symmetry containing the PtP axis be introduced by a fluxional process. For this to occur the following three processes must be fast on the n.m.r. time scale: (1) inversion at the sulphur *trans* to phosphorus; (2) inversion at the sulphur *trans* to X; and (3) flipping of the molecule about the S–S axis as shown below.

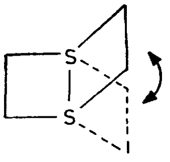


TABLE 1

Hydrogen-1 n.m.r. spectra of the dimers in dichloromethane solution

	PCH_3 groups[a]			SCH_3 *trans* to phosphine[a]			SCH_3 *cis* to phosphine[a]	
Complex	$\frac{\delta}{\text{p.p.m.}}$	$\frac{{}^2J(PH)}{Hz}$	$\frac{{}^3J(PtH)}{Hz}$	$\frac{\delta}{\text{p.p.m.}}$	$\frac{{}^4J(PH)}{Hz}$	$\frac{{}^3J(PtH)}{Hz}$	$\frac{\delta}{\text{p.p.m.}}$	$\frac{{}^3J(PtH)}{Hz}$
$[Pt_2Cl_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$	1.76 (d)	12	38					
cis-$[Pt_2Cl_2(PMe_2Ph)_2(\mu\text{-}SMe)_2]$	1.75 (d)	10.5	32	2.33 (t)	6	32	1.93 (s)	64
	1.72 (d)	10.5	32					
cis-$[Pt_2I_2(PMe_2Ph)_2(\mu\text{-}SMe)_2]$	1.95 (d)	10.5	33	2.85 (t)	6	35	1.94 (s)	64
	1.87 (d)	10.5	33					
cis-$[Pt_2Me_2(PMe_2Ph)_2(\mu\text{-}SMe)_2]$[b]	1.67 (d)	10.2	40	2.14 (t)	5	40	2.09 (s)	25
cis-$[Pt_2Ph_2(PMe_2Ph)_2(\mu\text{-}SMe)_2]$	1.55 (d)	10	39	1.09 (t)	5	43	2.14 (s)	22

	PCH_3 groups			SCH_2CH_3 groups		SCH_2CH_3 groups
	$\frac{\delta}{\text{p.p.m.}}$	$\frac{{}^2J(PH)}{Hz}$	$\frac{{}^3J(PtH)}{Hz}$	$\frac{\delta}{\text{p.p.m.}}$	$\frac{{}^3J(HH)}{Hz}$	(δ/p.p.m.)
cis-$[Pt_2Cl_2(PMe_2Ph)_2(\mu\text{-}SEt)_2]$	1.86 (d)	11	32	1.47 (t)	8	3.07 (c)
	1.74 (d)	11	32	0.95 (t)	8	
cis-$[Pt_2Me_2(PMe_2Ph)_2(\mu\text{-}SEt)_2]$[c]	1.64 (d)	10	40	1.25 (t)	7	2.57 (c)
				1.03 (t)	7	

[a] s = Singlet, d = doublet, t = triplet, c = complex multiplet. [b] δ(MePt) 0.29 p.p.m. (d) [$^3J(PH)$ 4, $^2J(PtH)$ 64 Hz]. [c] δ (MePt) 0.29 p.p.m. (d) [$^3J(PH)$ 5, $^2J(PtH)$ 72 Hz].

Inversion at sulphur in thiol complexes of Pt^{II} has been observed previously, and a mechanism involving synchronous cleavage of the PtS bond together with interaction of the lone-pair electrons on sulphur with platinum to form a new PtS bond has been proposed.[11–14] Part of the evidence rests on the observation that coupling between ^{195}Pt and protons on the thiol ligand was not lost during the fluxional process. We observe coupling of the μ-SMe protons to both ^{195}Pt centres for all the complexes (1a)—(1d) as described earlier. Thus the fluxional process must be intramolecular and cannot occur, for example, by reversible dissociation of (1) to monomeric species. A concerted mechanism, as for other thiol complexes of Pt^{II}, is likely.

The rate of inversion at sulphur in the molecules $[PtX_2(EtSCH_2CH_2SEt)]$ has been found[14] to increase with increasing *trans*-influence of X, the n.m.r. coalescence temperature being 85 °C when X = Cl, 50 °C when X = I, and −70 °C when X = Ph at 100 MHz. Thus the observation that two doublets due to PCH_3 protons are observed for (1) when X = Cl or I but only one doublet when X = Me or Ph suggests that inversion about the sulphur atom *trans* to X [process (2) above] may be the slow process for (1a), (1b), and (1e). It is possible that processes (1) and (3) may be fast on the n.m.r. time scale even at low temperatures, or that two or all three of the necessary processes may take place in unison. For example, a system in which process (1) is rapid at all temperatures and processes (2) and (3) take place together can be envisaged. This would explain why *syn* and *anti* isomers with respect to the two sulphur atoms in (1) cannot be detected, although such isomerism has been observed in some related complexes.[15]

Reactions with Methyl Halides.—Methyl iodide did not react with (1b) but did react with the organoplatinum complexes (1c), (1d), and (1f). In some cases the reactions took place in several stages as shown by preliminary studies in which the course of the reactions was monitored by recording changes in the ^1H n.m.r. spectra with time.

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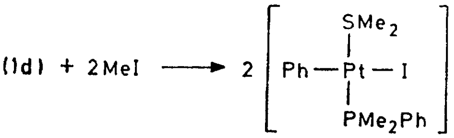
Reaction of MeI with (1d) took place according to equation (1). The n.m.r. spectrum (Table 2) of the product contained two resonances of equal intensity due to the SCH_3 and PCH_3 protons, each split into a 1 : 1 doublet due to coupling with ^{31}P and with satellites due to coupling with ^{195}Pt. In particular, the ^{195}Pt satellites were of a quarter of the intensity in each case, showing that the thioligand was no longer bridging between two platinum atoms. The similar reaction with CD_3I gave $[PtPhI(PMe_2Ph)\{SMe(CD_3)\}]$ which gave an n.m.r. spectrum which differed only in the relative intensities of the PCH_3 and SCH_3 signals which were now 2 : 1 as expected.



(1)

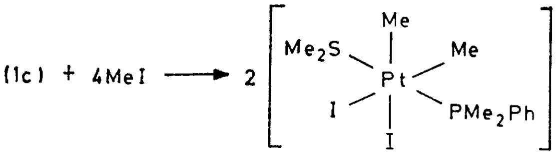
TABLE 2

Hydrogen-1 n.m.r. spectra of the products of reaction with methyl halides

Complex	δ(MeS) p.p.m.	^4J(PH) Hz	^3J(PtH) Hz	δ(MeP) p.p.m.	^2J(PH) Hz	^3J(PtH) Hz	δ(MePt) p.p.m.	^3J(PH) Hz	^2J(PtH) Hz
$[PtPhI(PMe_2Ph)(SMe_2)]$	2.12 (d)	3.6	40	2.64 (d)	10.8	46			
$[Pt_2Me_4I_2(PMe_2Ph)_2(\mu\text{-}SMe)_2]$	(c)				(c)		1.23 (d)	4.5	72 [a]
							0.95 (d)	3.3	62 [b]
$[Pt_2Me_2(CD_3)_2I_2(PMe_2Ph)_2(\mu\text{-}SMe)_2]$	(c)				(c)		0.97 (d)	3.3	62 [b]
$[PtMe_2I_2(PMe_2Ph)(SMe_2)]$	2.77 (d)	5	25	2.60 (d)	11.5	26	1.37 (d)	3.5	65 [b]
$[PtMe_2I_2(PMe_2Ph)_2]$				2.39 (t)	7.5	20	0.80 (t)	5.5	66 [a]
$[Pt_2Br_2Me_4(PMe_2Ph)_2(\mu\text{-}SMe)_2]$	(c)				(c)		0.94 (d)	3.0	68 [a]
							0.75 (d)	1.5	59 [b]
$[PtBr_2Me_2(PMe_2Ph)(SMe_2)]$	2.58 (d)	5	24	2.31 (d)	12	26	1.01 (d)	3	66 [a]

[a] Methyl group *trans* to halogen. [b] Methyl group *trans* to sulphur.

The reactions of methyl halides with (1c) were considerably more complex. Thus reaction took place in two clear stages, and the products were difficult to purify since they occluded solvent very strongly. The reaction with methyl iodide gave finally the product of equation (2). The n.m.r. spectrum of the product contained three doublets of equal intensity due to the $PtCH_3$, SCH_3, and PCH_3 protons, all split by coupling to ^{31}P. Addition of PMe_2Ph to this product caused a change in the n.m.r. spectrum with a singlet due to SMe_2 appearing at δ 2.08 p.p.m. together with the characteristic spectrum of (3).[2] The reaction of CD_3I with (1c) gave a product with a similar n.m.r. spectrum but with relative intensity $PCH_3 : SCH_3 : PtCH_3$ of 2.0 : 1.2 : 0.8.



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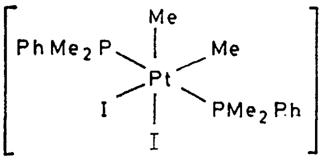
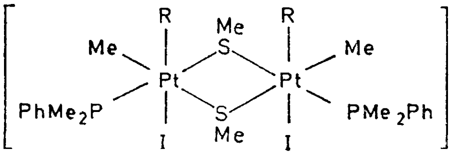
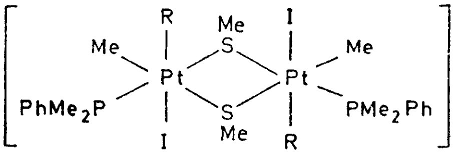


(3)

The initial reaction of methyl iodide with (1c) took place very rapidly to give the product of oxidative addition, $[Pt_2Me_4I_2(PMe_2Ph)_2(\mu\text{-}SMe)_2]$. Thus the n.m.r. spectrum contained two methylplatinum resonances of equal intensity at δ 1.23 and 0.95 p.p.m. with coupling constants ^2J(PtH) of 72 and 62 Hz respectively (Table 2). This is consistent with structure (4a) or (5a) with methylplatinum groups *trans* to iodide and sulphur respectively.[2-5]. The peaks due to the SCH_3 and PCH_3 protons overlapped and could not be assigned with confidence. Addition of CD_3I to (1c) gave a product whose n.m.r. spectrum contained only one methylplatinum peak at δ 0.97 p.p.m. with ^2J(PtH) 62 Hz.



(4a) R = Me
(4b) R = CD_3



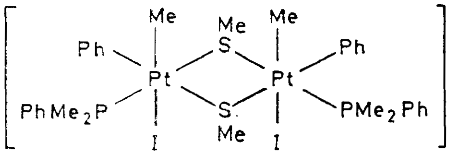
(5a) R = Me
(5b) R = CD_3

This suggests that *trans*-oxidative addition to give (4b) or (5b) has occurred. *trans*-Oxidative addition of CD_3I to *cis*-$[PtMe_2(PMe_2Ph)_2]$ has been established previously.[4] In solution the complex (4) or (5) decomposed slowly as evidenced by changes in the n.m.r. spectra. In the presence of methyl iodide, (4a) or (5a) gave $[PtMe_2I_2(PMe_2Ph)(SMe_2)]$ after several days, but the products formed in the absence of MeI could not be identified.

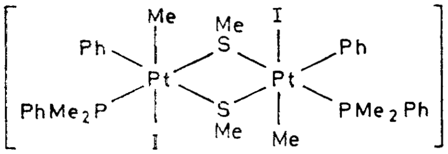
Reaction of methyl bromide with (1c) took place in a similar way to give first $[Pt_2Br_2Me_4(PMe_2Ph)_2(\mu\text{-}SMe)_2]$ and then $[PtBr_2Me_2(PMe_2Ph)(SMe_2)]$ as evidenced by the n.m.r. spectra (Table 2). In this case the products were particularly difficult to purify, however, and we were unable to obtain satisfactory analytical data for the final product.

DISCUSSION

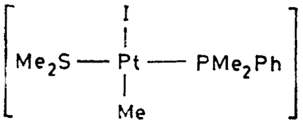
The reaction of (1d) with MeI to give $[PtPhI(PMe_2Ph)(SMe_2)]$ could take place either by oxidative addition of methyl iodide to both platinum(II) centres to give (6a) or (6b) followed by reductive elimination by cleavage of the Pt–S and Pt–Me bonds, or by direct nucleophilic attack by the lone pair of the bridging sulphur ligand on MeI followed by rearrangement. Since no intermediate dimeric products were observed the mechanisms cannot be distinguished. However, the reaction of MeI with (1c) clearly takes place to give initially the product of oxidative addition, (4a) or (5a). The final product is then formed first by reductive elimination to give [PtMeI(PMe$_2$Ph)(SMe$_2$)], (7), followed by further oxidative addition of methyl iodide to give [PtMe$_2$I$_2$(PMe$_2$Ph)(SMe$_2$)]. The different reactions of (1c) and (1d) can be understood in terms of the relative stabilisation of oxidation state IV relative to II for platinum in methylplatinum compared to phenylplatinum complexes.[5] Thus with (1c) initial oxidative addition of MeI is rapid, and the product (4a) or (5a) undergoes reductive elimination only slowly to give (7) which rapidly undergoes further oxidative addition. However, oxidative addition to (1d) is much slower and the presumed intermediate (6) rapidly undergoes reductive elimination to give [PtPhI(PMe$_2$Ph)(SMe$_2$)] which does not react further with methyl iodide. In the reductive-elimination step the methyl–platinum bond is cleaved selectively rather than the phenyl–platinum bond, as expected by analogy with earlier work.[3-5,16]



(6a)

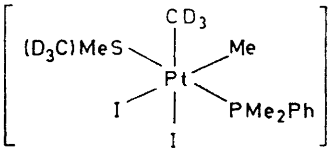


(6b)



(7)

Further information about the reductive-elimination reaction of (4) was obtained by thermal decomposition of the final product [PtMe$_2$I$_2$(PMe$_2$Ph)(SMe$_2$)]. This gave a mixture of ethane, methyl iodide, and dimethyl sulphide which could be identified by g.l.c.–mass spectrometry. Decomposition of the final product from reaction of (1c) with CD$_3$I gave C$_2$D$_6$ and CH$_3$CD$_3$ in relative proportion 1 : 2.1 and MeI and CD$_3$I in relative proportion 1 : 2.0. This indicates that the product is a 2 : 1 mixture of (8) and (9). This is also in good agreement with the conclusions from the n.m.r. data. Thus a 2 : 1 mixture of (8) and (9) would give on integration PCH$_3$: SCH$_3$: PtCH$_3$ = 2 : 1.3 : 0.7 which compares with the observed ratio of 2 : 1.2 : 0.8. In the reductive elimination of (4b) or (5b) therefore it seems that cleavage of CD$_3$ groups (*trans* to iodide) to give finally (8) takes place twice as fast as cleavage of methyl groups (*trans* to sulphur) to give finally (9).



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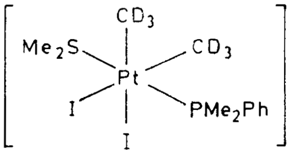

(9)

EXPERIMENTAL

General techniques and the separation and identification of volatile products by g.l.c.–m.s. have been described previously.[3,4,16] Molecular weights were determined by osmometry in chloroform solution.

[Pt$_2$Cl$_2$(μ-Cl)$_2$(PMe$_2$Ph)$_2$].—This complex was prepared by heating under reflux a mixture of PtCl$_2$ (0.70 g) and *cis*-[PtCl$_2$(PMe$_2$Ph)$_2$] (1.40 g) in 1,1,2,2-tetrachloroethane (50 cm^3) for 6 h. The solution was filtered, the volume of the filtrate reduced to 10 cm^3, and pentane (25 cm^3) was added to precipitate the product, yield 2.07 g, m.p. 205—220 °C (lit.,[7] 215—230 °C).

cis-Di-μ-methylthio-bis[chloro(dimethylphenylphosphine)-platinum(II)], (1a).—A solution of [Pt$_2$Cl$_2$(μ-Cl)$_2$(PMe$_2$Ph)$_2$] (2.1 g) in dichloromethane (30 cm^3) was saturated with methanethiol and the mixture was stirred for 5 d. Methanethiol was passed through the solution occasionally during this time. Evaporation of the solvent and recrystallisation from methanol gave the pure white crystalline *product*, yield 1.7 g (83%), m.p. 196—198 °C (Found: C, 26.7; H, 3.6. Calc. for $C_{18}H_{28}Cl_2P_2Pt_2S_2$: C, 26.0; H, 3.4%). Complex (1e), *cis*-[Pt$_2$Cl$_2$(PMe$_2$Ph)$_2$(μ-SEt)$_2$], was prepared similarly, yield 77%, m.p. 174—175 °C (Found: C, 27.8; H, 3.95. Calc. for $C_{20}H_{32}Cl_2P_2Pt_2S_2$: C, 27.9; H, 3.7%).

Complex (1b), cis-[Pt$_2$I$_2$(PMe$_2$Ph)$_2$(μ-SMe)$_2$].—A mixture of sodium iodide (0.5 g) in water (20 cm^3) and (1a) (0.23 g) in CH$_2$Cl$_2$ (10 cm^3) was stirred for 24 h. The *product* was obtained by evaporation of the dried organic layer and was recrystallised from dichloromethane–hexane, yield 0.24 g (90%), m.p. 192—196 °C (Found: C, 21.5; H, 2.9%; *M*, 1 031. Calc. for $C_{18}H_{28}I_2P_2Pt_2S_2$: C, 21.3; H, 2.8%; *M*, 1 014).

Complex (1c), *cis*-[Pt$_2$Me$_2$(PMe$_2$Ph)$_2$(μ-SMe)$_2$].—Methyllithium (0.6 cm^3, 2.1 mol dm^{-3} solution in diethyl ether) was added to (1a) (0.4 g) in diethyl ether (15 cm^3). After 30 min the mixture was hydrolysed with ammonium chloride solution, and the *product* was obtained by evaporation of the dried organic layer as a colourless oil. It could be crystallised from acetone, yield 0.26 g (78%), m.p. 124—127 °C (Found: C, 29.4; H, 4.4. Calc. for $C_{20}H_{34}P_2Pt_2S_2$: C, 30.4; H, 4.3%). The following *complexes* were prepared

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[16] M. P. Brown, A. Hollings, K. J. Houston, R. J. Puddephatt, and M. Rashidi, *J.C.S. Dalton*, 1976, 786.

similarly: *cis*-[$Pt_2Me_2(PMe_2Ph)_2(\mu\text{-}SEt)_2$], (1f), yield 80%, m.p. 78—80 °C (Found: C, 31.5; H, 4.7. Calc. for $C_{22}H_{38}P_2Pt_2S_2$: C, 32.3; H, 4.65%); *cis*-[$Pt_2Ph_2(PMe_2Ph)_2(\mu\text{-}SMe)_2$], (1d), from (1a) and phenylmagnesium bromide, yield 80%, m.p. 140—145 °C (Found: C, 41.2; H, 4.4. Calc. for $C_{30}H_{38}P_2Pt_2S_2$: C, 39.4; H, 4.2%).

(*Dimethylphenylphosphine*)(*dimethyl sulphide*)(*iodo*)*phenylplatinum*(II), [$PtPhI(PMe_2Ph)(SMe_2)$].—Methyl iodide (1 cm³) was added to a solution of *cis*-[$Pt_2Ph_2(PMe_2Ph)_2(\mu\text{-}SMe)_2$] (0.1 g) in CH_2Cl_2 (5 cm³). After 24 h the volume was reduced and hexane was added to precipitate the *product*, yield 0.12 g (92%), m.p. 234–235 °C (decomp.) (Found: C, 31.5; H, 3.4. Calc. for $C_{16}H_{22}IPPtS$: C, 32.05; H, 3.4%).

(*Dimethylphenylphosphine*)(*dimethyl sulphide*)*di-iododimethylplatinum*(IV), [$PtMe_2I_2(PMe_2Ph)(SMe_2)$].—A solution of (1c) (0.08 g) in MeI (5 cm³) was allowed to stand at room temperature for 5 d. A yellow solid slowly crystallised during this time, yield 0.10 g (77%), m.p. 144—146 °C (decomp.) (Found: C, 21.0; H, 4.2. Calc. for $C_{12}H_{23}I_2PPtS$: C, 21.2; H, 3.4%).

Di-μ-methylthio-bis[(*dimethylphenylphosphine*)*iododimethylplatinum*(IV)], [$Pt_2Me_4I_2(PMe_2Ph_2)(\mu\text{-}SMe)_2$].—Methyl iodide (4 cm³) was added to (1c) (0.20 g) to give a yellow solution. After 5 min, the solvent was evaporated *in vacuo*, and the product was washed thoroughly with diethyl ether and dried *in vacuo*, yield 0.18 g (85%), m.p. 115—125 °C (decomp.) (Found: C, 26.0; H, 4.2%; *M*, 1 057. Calc. for $C_{22}H_{40}I_2P_2Pt_2S_2$: C, 24.6; H, 4.0%; *M*, 1 074).

[$Pt_2Br_2Me_4(PMe_2Ph)_2(\mu\text{-}SMe)_2$].—Methyl bromide (5 cm³) was added to (1c) (0.30 g) in a Pyrex tube. The tube was sealed and was set aside at 35 °C for 25 min. It was then opened and the MeBr was evaporated *in vacuo* to give the *product*, which was washed with diethyl ether and dried *in vacuo*, yield 0.25 g (70%), m.p. 125—130 °C (decomp.) (Found: C, 27.1; H, 4.3. Calc. for $C_{22}H_{40}Br_2P_2Pt_2S_2$: C, 26.9; H, 4.1%).

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